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SURFACE AND MICROANALYTICAL STUDIES OF WHETLERITE CHARCOALS: 1. EFFECTS OF AGING

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Abstract—ASC Whetlerite charcoals impregnated with copper and chromium have been studied by several surface and microanalytical techniques to determine the effects of aging on the composition and microstructure. X-ray photoelectron spectroscopic (XPS) studies of absorbers not deliberately aged, showed that most of copper on the inside of each particle was present as Cu(I). Transmission microscopy showed that some of this copper is present as crystallites with diameters up to 0.1 μm. Natural or artificial aging in a humid atmosphere resulted in the number and size of such crystallites and a migration of some of the copper impregnants to the outer surface of the particle, where it is bonded largely as $Cu(OH)_2$. Chromium is present in the adsorber in both Cr(III) and Cr(VI) oxidation states and it undergoes little change during aging.

Key Words—Whetlerite charcoals, aging, XPS, STEM.

1. INTRODUCTION

Whetlerite impregnated charcoals were developed during World War I as adsorbents for toxic gases. The charcoal is typically prepared by impregnation with ammoniacal carbonate solutions of copper (II) and chromium (VI) salts[1]. Such a charcoal in fresh condition reacts irreversibly and rapidly with gases, such as cyanogen chloride and hydrogen cyanide, to produce ammonia and ammonium chlorides through a variety of intermediates[2]. It has been shown that the copper and chromium salts present exhibit a synergistic effect in reacting with cyanogen chloride[3]. For lack of evidence to the contrary, it has been presumed in the past that the major catalytic or absorptive active species was a cupric chromate on the carbon surface. More recently, however, there is some evidence that Cu(I) and Cr(III) are also major chemical species present[4–5]. Previous studies, particularly those using transmission electron microscopy[5], have shown small particles of adsorbent distributed within the structure of the charcoal. However, the composition of such particles and their effect on reaction has not yet been assessed.

The capacity of the impregnated charcoal for absorbing ClCN is strongly dependent on the moisture content of the surface. Long exposure to moisture (1–2 years), decreases the capacity markedly. Such effects have previously been ascribed to the increase of copper-chromium crystallite size and the corresponding reduction in overall surface area[6].

In this study, several normal and aged Whetlerite charcoals have been examined using microscopic and surface analytical techniques to determine: (a) the chemical nature of the crystallites in the charcoal matrix, (b) the changes which occur when the impregnated charcoal is subjected to normal aging procedures, as well as to accelerated tests designed to evaluate charcoal response to moisture within a period of a few thousand hours.

2. EXPERIMENTAL

2.1 *Materials*

ASC Whetlerite was prepared by impregnating BPL-activated carbon particles (mean diameter 0.5 mm) with an aqueous solution (12% NH_3), buffered by 10.9% carbonate ion and containing 9% cupric copper and 4% chromate ion[7]. The prepared specimens were stored for several months under dry nitrogen until use. As such, they are typical of absorbers ready for field use and are so designated.

Two types of aging tests were used. Natural aging was done by leaving the charcoal exposed to ambient laboratory air for 597 days, while accelerated aging took place in steady air flow humidity cabinet at 45°C and a relative humidity of 80%. Two specimens rapidly aged for 14 days and 28 days were analyzed and compared with the samples naturally aged for periods of ~2 years.

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2.2 *Analytical techniques*

X-ray photoelectron spectroscopy was done in a Surface Science Laboratories SSX–100 spectrometer using monochromatized AlKα exciting X-radiation. Quantitative measurements were obtained from integrated peak intensities corrected with Scofield photoelectron cross-sections[8]. Exterior surfaces of the charcoal particles were analyzed by gently mounting a number of them on 3M copper conducting tape. The interior composition of these same particles was determined by mechanically crushing the particles onto the tape. No contribution from the underlying tape was detected. Each particle surface was analyzed individually with a precision of ±20% for the copper and chromium concentrations.

For Scanning Transmission Electron Microscopy (STEM), samples were prepared by pulverizing the charcoal in a mortar and pestle, ultrasonic cleaning in water, and drying onto a gold mesh (#200), previously coated with Formvar and carbon. The Phillips 400 microscope was run at 80 kV with a beam current of 80 μA and a 50 μm condensor aperture. X-ray analysis was done with an energy dispersive X-ray (EDX) system using a low background beryllium window. X-ray data was corrected for thin section effects.

Ion microscopy was carried out on flat surfaces of Whetlerite particles using a Cameca IMS–3f Secondary Ion Mass Spectrometer. A primary ion beam of cesium was used. Ion images were collected, digitized, and processed on a computer-aided facility developed in this laboratory. All images were taken from a 150 μm diameter area.

Scanning electron microscopy was done using an ISI DS–130 microscope using a 30 kev primary beam.

3. RESULTS

3.1 *X-ray photoelectron spectroscopy*

XPS spectra of both crushed and uncrushed Whetlerite charcoals and charcoals aged by different methods all showed the presence of copper, chromium, carbon, and oxygen. In addition, minor elements such as silver, silicon, aluminum, and phosphorous were often detected. A detailed XPS spectrum of a crushed "field" Whetlerite surface is shown in Fig. 1. "Field" specimens are those taken out of normal dry storage conditions, usually after a period of several months. The intensities were corrected for photoelectron cross-section and for the analyzer transmission, and relative concentrations were determined using the manufacturer's standard program. In Table I, the surface compositions of crushed and uncrushed specimens of Whetlerite are compared for "field" specimens, as well as those exposed to natural and accelerated aging tests, and a non-impregnated charcoal.

The composition of copper on the crushed "field" Whetlerite surface (~1%) was considerably lower than that expected for the bulk composition (7% Cu_2O, 4% Cr_2O_3, balance-carbon). In naturally aged specimens, the surface copper composition of the particle was sharply higher than the composition on the unreacted "as received" specimen. Crushing of the particle reduced, but did not entirely eliminate, the apparent enrichment.

Natural aging for a two-year period results in a substantial increase in the copper concentration on the outermost surface, and this was found to be consistent for a number of specimens analyzed. In general, aging of any sort was found to result in a graded increase in the surface concentration of both copper

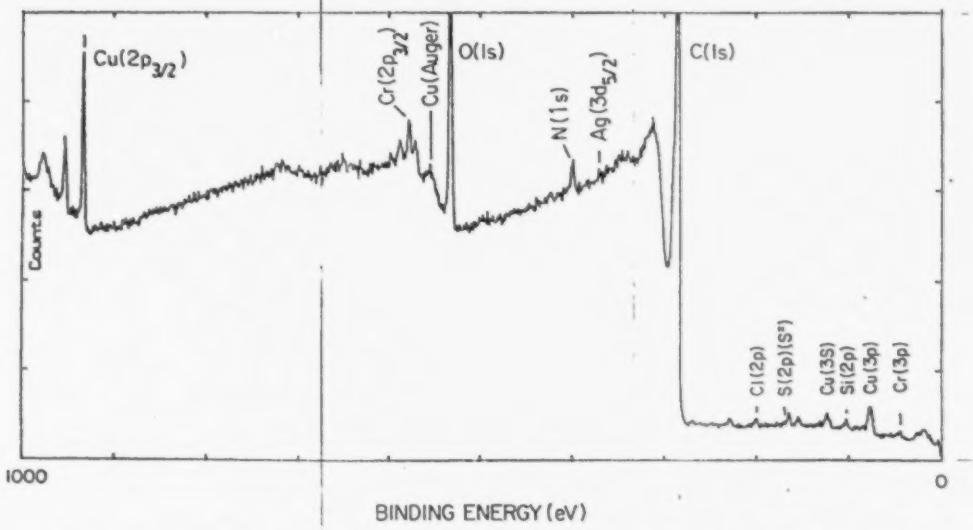

Fig. 1. Wide energy range XPS spectrum of the surface of an "as received" Whetlerite charcoal that had been mechanically crushed to reveal the interior of the charcoal particles.

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Table 1. Surface composition of charcoal adsorbents studied as determined by XPS (% of atomic)

Sample	Cr* (3p)	Cu* (3p)	Ag (3d)	C (1s)	O (1s)	N (1s)	Cl (2p)	Si (2p)	S* (2p)	SO_4^{2-} (2p)	Cr(III)/Cr(Total)	Cu(I)/Cu(Total)
Unimpregnated charcoal (crushed)	—	—	—	95.	3.9	0.03	0.03	0.3	0.3	—	—	—
Whetlerite, "field" (whole)	0.6	1.7	0.03	87.	12.	1.5	0.2	1.2	0.7	0.2	0.7	0.3
Whetlerite, "field" (crushed)	0.4	0.9	0.03	89.	7.4	1.0	0.1	0.5	0.4	0.03	0.6	0.95
Whetlerite, naturally aged (whole)	5.	2.	—	70.	22.	—	—	—	—	—	0.7	0.2
Whetlerite, naturally aged (crushed)	2.	1.3	—	77.	20.	—	—	—	—	—	0.7	0.5
Whetlerite, artificially aged (whole)	2.	1.2	—	77.	20.	—	—	—	—	—	0.7	0.3
Whetlerite, artificially aged (crushed)	1.	0.7	—	81.	18.	—	—	—	—	—	0.7	0.7

*Cu(3p) and Cr(3p) lines are measured, since they sample a greater depth than their 2p analogues and are therefore less prone to the effects of local surface contamination.

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and chromium. There was, however, no correlation found between aging and the copper/chromium concentration ratio.

In Fig. 2, the Cu($2p_{3/2}$) spectra are compared for copper detected in two conditions, which resulted in very different chemical structures for the element. A spectrum for copper in the interior of an "as received" pellet specimen (obtained by crushing the charcoal pellets) is shown in Fig. 2(a). The major narrow Cu($2p_{3/2}$) line indicates that all copper is bonded in the Cu(I) state, probably as Cu_2O[9]. The minor line chemically shifted to higher binding energy is ascribed to a small concentration of Cu(II). By contrast, a spectrum of the surface of a naturally-aged specimen showed a very different Cu($2p_{3/2}$) line structure, which is resolved in Fig. 2(b). In addition to the singlet peak at 932.5 eV, ascribed to Cu(I), an additional complex line structure is ascribed to Cu(II). This consists of a chemially-shifted, broadened principal line, represented by the two peak shapes at 933.3 eV and 934.5 eV, and a complex shake-up lineshape. On the basis of previous studies, the Cu(II) component is assigned to $Cu(OH)_2$[9]. This species is clearly distinguishable from another possible cupric species, CuO. Although earlier XPS studies[2] identified $CuCrO_4$ on Whetlerite surfaces, their published Cu(2p) spectrum is identical to that for $Cu(OH)_2$. In our case, the measured Cu/Cr ratios precluded $CuCrO_4$ as a possible compound. All Cu(II) species detected on our specimens are identified as CuO and/or $Cu(OH)_2$. The relative Cu(I)/Cu(II) concentrations on all surfaces analyzed are reported in Table 1.

The detailed Cr($2p_{3/2}$) spectra are shown in Fig. 3 for the same specimens discussed above. These spectra are resolved into Cr(III) and Cr(VI) components on the basis of previous studies[10] of the chromium oxygen system: Cr(III) is a broad complex

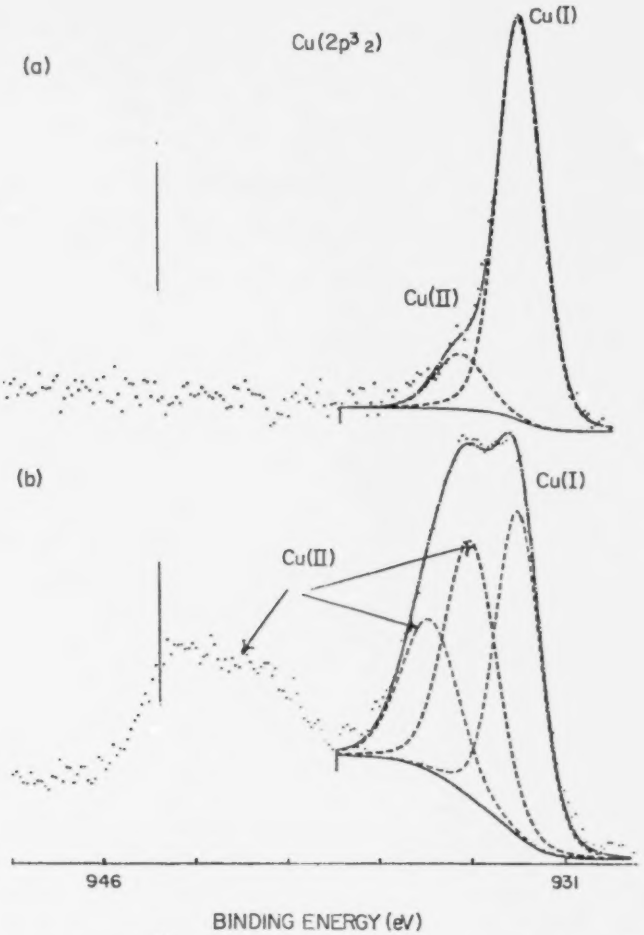

Fig. 2. Detailed Cu($2p_{3/2}$) XPS spectra of (a) a crushed "as received" Whetlerite surface; (b) a Whetlerite particle surface exposed to natural aging for 2 years.

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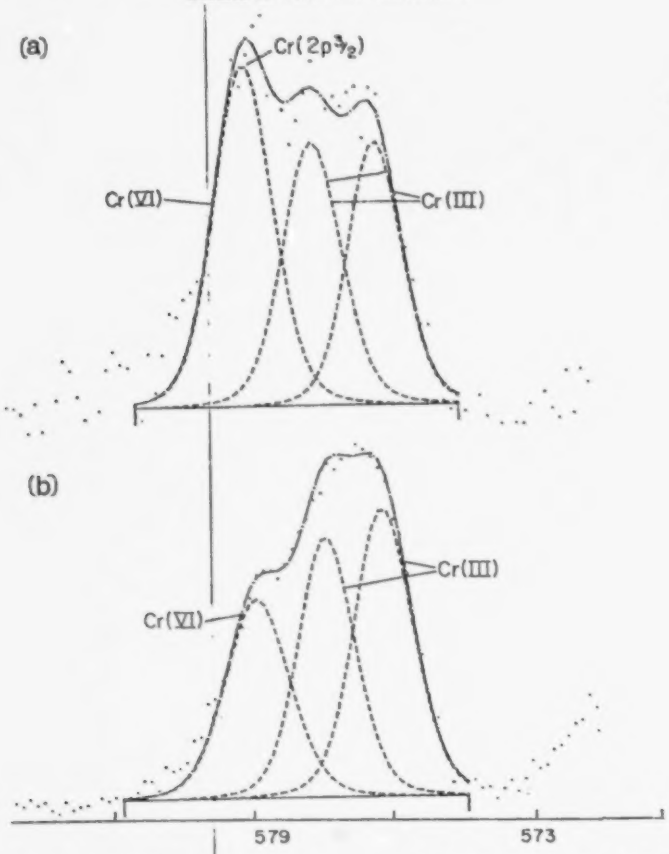

Fig. 3. Detailed Cr($2p_{3/2}$) XPS spectra of (a) a crushed "as received" Whetlerite surface; (b) a Whetlerite particle surface exposed to natural aging for 2 years.

system of peaks, of which the major intensity is centred at 576.5–577.0 eV; Cr(VI) is a considerably narrower peak centred at 579.0 eV. Curve fitting of the Cr($2p_{3/2}$) line, on this basis, for the interior of an "as received" specimen, Fig. 3(a), shows that both Cr(VI) and Cr(III) are present in approximately equal proportions on the basis of peak area. For the naturally aged surfaces, Fig. 3(b), there is a small increase in the relative amount of the Cr(III) component. Cr(III)/Cr(VI) ratios are given for all specimens in Table 1.

Spectra of the C(ls) spectra (not shown) indicate that "graphitic" or "inorganic" carbon is the only detectable carbon species for all specimens studied.

It appears, then, that most copper present in a "field" Whetlerite specimen is in the cuprous, Cu(I), oxidation state. Continued exposure to the atmosphere results in its oxidation to Cu(II), probably largely as $Cu(OH)_2$. Under the same unexposed conditions, the chromium is bonded as both Cr(III) and Cr(VI). Air exposure results in some additional reduction to Cr(III).

3.2 *Scanning electron microscopy*

Scanning electron micrographic (SEM) comparison were made between "as received" charcoal surfaces and those subjected to rapid and natural aging procedures. No significant qualitative difference in particle size or shape could be discerned between the different treatments, nor could any apparent change in surface area be detected. Only one specimen, rapidly aged for several months, was found to exhibit any surface alteration detectable by SEM. In this latter case, the surface was covered with acicular crystals (not shown). Other workers[11] have also noted the growth of needle and spheroidal crystals on aged charcoals. Energy dispersive microscopic analysis of the particles was unable to identify any local variations in copper or chromium concentration.

3.3 *Ion microscopy*

Secondary ion images of the distributions of $^{63}Cu^-$, $^{52}Cr^-$, $^{28}Si^-$ and $^{27}Al^-$ are shown in Fig. 4(a)–(d). Images for $^{12}C^-$ and $^{32}S^-$ (not shown) are featureless.

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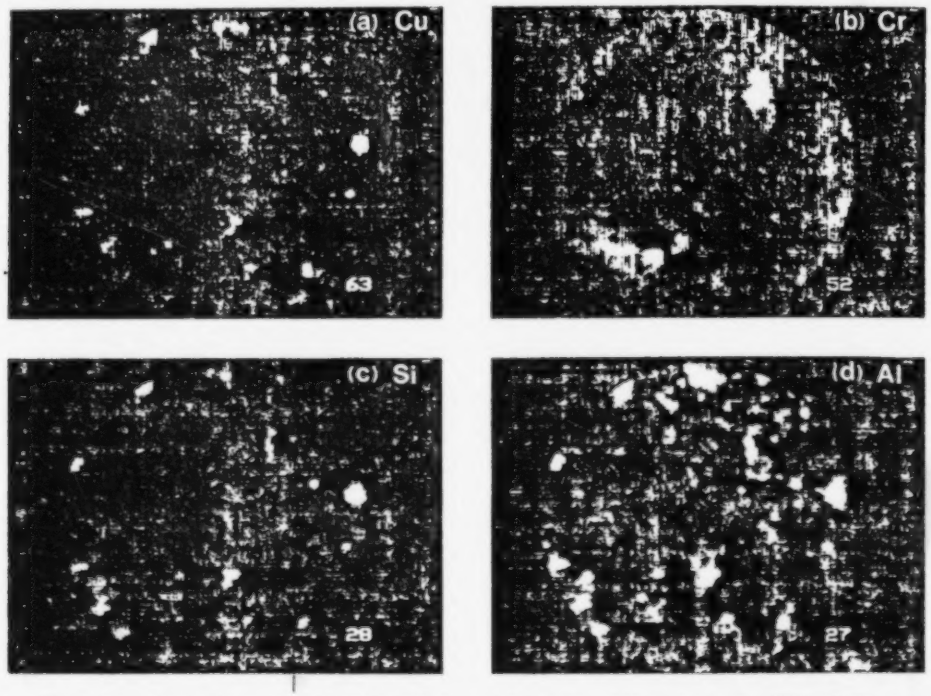

Fig. 4. Ion microscope images showing inorganic element distribution within an "as received" Whetlerite particle.

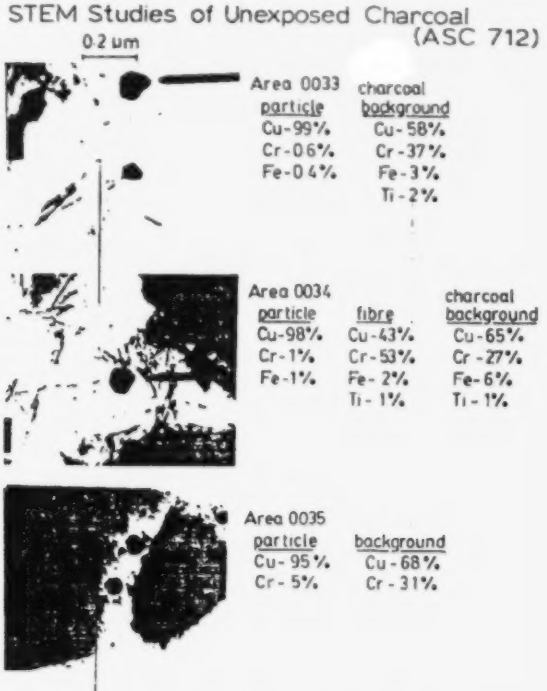

Fig. 5. Scanning transmission electron micrographs and related X-ray microanalyses of areas on a freshly impregnated charcoal.

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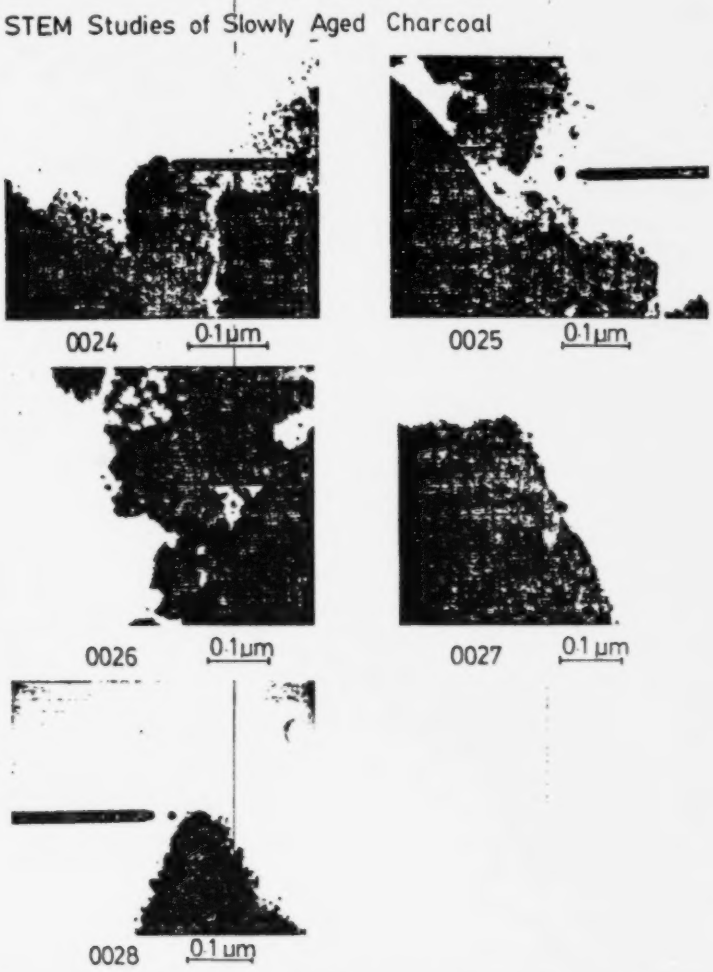

Fig. 6. Scanning transmission electron micrographs and related X-ray microanalyses of a naturally aged impregnated charcoal.

Both copper and chromium are seen to be localized with the same areas a few microns in diameter. In addition, however, a more generalized distribution of chromium can be recognized.

3.4 *Transmission electron microscopy*

Analytical Scanning Transmission Electron Microscopy (STEM) was found to be the only method capable of detecting structural changes in the charcoal due to the previously described aging procedures. One previous TEM study[4] has already identified the presence of certain sub-micron particles in the charcoal, but no elemental analysis could be made. X-ray diffraction studies have also suggested the presence of copper-rich crystallites, at least in charcoals which have been subjected to aging.

Figure 5 shows high magnification TEM micrographs of three areas on an "as received" Whetlerite charcoal surface. A number of crystals of size 0.095–0.1 μm diameter are clearly detected, along with a distribution of smaller particles down to 0.005 μm diameter. Many of the particles are joined by fibre-like lines (~5 nm in diameter). The EDX analyses are also shown for each particle indicated in the image by the pointer. In addition, an analysis for the background near each particle analyzed is shown. Areas 0033 and 0034 shown, in particular, the crystalline nature of the particles present and the detail of the "fibrous" structure. The EDX result shows that each crystal indicated has a copper concentration of >95%, considering, of course, only the elements detectable by EDX. The background, by contrast, has approximately equal concentrations of chromium and copper. In area 0034, the composition of the fibre-like line was also able to be analyzed and it was found to be enriched in chromium.

Analysis of the naturally aged impregnated char-

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Table 2. Elemental composition of particles in aged impregnated charcoals from STEM-EDX measurements

A. Naturally Aged Specimen

	Spot Composition (%)					Background Composition (%)				
Area	Cu	Cr	Fe	Ti	Other	Cu	Cr	Fe	Ti	Other
0015	77	17	3	—	Ca	66	33	—	—	—
0017	79	20	—	—	—	60	33	3	—	Cu
0018	76	20	2	—	Ca	61	38	—	—	—
0020	80	20	—	—	—	56	38	4	—	—
0024	89	6	1	2	Cu	68	27	—	—	Cu
0026	90	6	1	1	Cu	33	15	—	—	Ca,K
0027	92	7	—	—	—	51	43	5	—	—

B. Rapidly Aged Specimen

	Spot Composition (%)					Background Composition (%)				
Area	Cu	Cr	Fe	Ti	Other	Cu	Cr	Fe	Ti	Other
0001	91	7	1	—	—	64	31	—	3	—
0002	85	14	—	—	—	60	34	5	—	—
0003	88	10	1	1	—	64	30	3	3	—
0004	74	23	2	—	—	57	33	5	5	—
0007	90	10	—	—	—	53	44	3	—	—

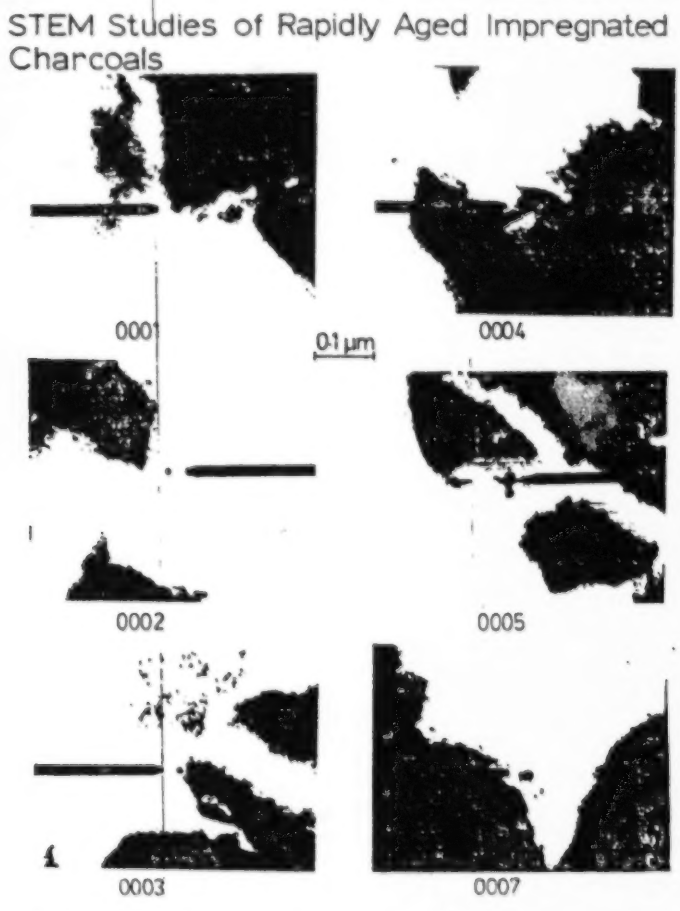

Fig. 7. Scanning transmission electron micrograph and related X-ray microanalyses of a rapidly aged impregnated charcoal.

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coal specimens by STEM revealed some dramatic differences. Figure 6 shows images of a number of areas which reveal a much smaller number of copper crystallites and a much smaller overall size for those remaining. With few exceptions, the mean particle diameter was <0.01 μm. A second major difference is the almost complete disappearance of the fibrous network. Only in a few areas (for example, areas 0027 and 0028 in Fig. 6), can any evidence of the fibrous structure still be seen.

X-ray analysis of the naturally aged charcoal (Table 2), suggests that the composition of the detectable particles remaining contained somewhat more chromium than did those in the fresh charcoal specimen. However, it should be noted that since the overall particle size is smaller, there is a greater possibility of including some of the background in any particle analysis. Also noted in this matrix is an increase in calcium, possibly carried into the matrix as an air particulate.

STEM images of the rapidly aged charcoal are shown in Fig. 7, with the corresponding X-ray microanalytical data shown in Table 2. Again, the overall density of copper crystallites was found to have decreased with respect to that in the fresh impregnated charcoal, and little or no evidence of any fibre-like lines could be seen. There were no differences observed in specimens exposed for 14 and 28 days.

From the above results, it is clear that the analytical STEM is one of the better approaches to provide unambiguous identification of the sub-micron features which appear to be involved in changes to the material during aging.

4. DISCUSSION

The combined result of this study have helped to provide new information on the chemical composition and microstructure of freshly prepared "field" Whetlerite charcoals. From XPS data, it has been shown that the copper is largely in the form of cuprous oxide, within a particle interior, but is oxidized to a Cu(II) form on its outer surface. The observation of copper largely in a Cu(I) state differs from reports of other authors[12,13]. The difference may be due to the longer storage time, under inert gas, of our specimens. On a microscopic scale, the copper is found to be present in crystallites from which chromium is largely excluded. These crystallites range in size from a 0.005 μm diameter to .01 μm, with the mean size about 0.02 μm. Fibre-like structures appear to connect many of the copper crystallites and these are found to be enriched in chromium. It is clear that the growth of the copper crystallites occur along such fibres (see area 0035 of Fig. 5). It is possible that the fibres represent the pore structure of the charcoal onto whose walls chromium oxide has been adsorbed, thus rendering the structure optically dense for detection in the transmission microscope. The surface of the pore may thus be a structurally preferential surface for nucleation and growth of single crystallites of a copper compound (probably cuprous oxide, according to the XPS evidence). The localized copper and chromium enrichments observed by ion microscopy represent areas much larger than those observed by transmission microscopy. It is assumed that the former represent localized precipitates of one element that caused the deposition of the other.

Aging, either natural or accelerated, appears to produce at least small quantities of cupric oxide or hydroxide in the matrix. From XPS quantitative measurements, there is evidence of a net movement of copper from the particle interior during aging to the near-surface region. Following accelerated aging for long periods, an enriched layer of cupric hydroxide was found on the outermost surface. There is also clear evidence that aging results in a sharp drop in the concentration of cuprous oxide crystallites in the matrix and, as well, the virtual disappearance of the fibrous network observed in the fresh specimen. The cuprous oxide crystallites appear to have decreased in number and size by the moisture, with a subsequent reprecipitation in an amorphous and less catalytically active form.

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DESCRIPTORS: (U) Activated carbon;Charcoal;Aging tests (materials);Humidity;X ray spectroscopy;Scanning electron microscopy;Surface properties;Copper organic compounds;Impregnating

IDENTIFIERS: (U) X-ray photoelectron spectroscopy

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